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ON THE FORMATION OF NITROGEN OXIDES IN THE COMBUSTION PROCESSES OF HYDROGEN IN AIR

LA FORMATION D'OXYDES D'AZOTE PAR LA COMBUSTION D'HYDROGENE DANS L'AIR

Carlos Sânchez-Tarifa
Juan R. Sanmartin
Enrique Fraga
INTA.- Madrid (Spain)

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Introduction

A research programme is being carried out at the Instituto Nacional de Têcnica Aeroespacial of Spain, on several aspects of the formation of nitrogen oxides in continuous flow combustion systems, considering hydrogen and hydrocarbons as fuels*.

The research programme is fundamentally oriented on the basic aspects of the problem, although it also includes the study of the influence on the formation process of several operational and design variables of the combusters, such as type of fuels, fuel/air ratio, degree of mixing in premixed type flames, existence of droplets as compared with homogeneous combustion, etc.

This problem of nitrogen oxides formation is receiving lately great attention, specially in connection with automobile reciprocating engines and aircraft gas turbines.

This is due to the fact of the increasing frequency and intensity of photochemical hazes or smog, typical of urban areas submitted to strong solar radiation, which are originated by the action on organic compounds of the oxidants resulting from the photochemical decomposition of nitrogen dioxide NO_2.

In the combustion process almost all nitrogen oxides are in form of NO. This nitric oxide reacts with the oxygen of the air and forms NO_2 , this reaction only taking place in or near the exhaust of the motors, since the $NO-O_2$ reaction becomes frozen for the concentration existing in the atmosphere.

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Nitric oxide formation has been experimentally studied in reciprocating engines and gas turbines. On the other hand, theoretical models are of a preliminary nature, since the chemical kinetics model for the reaction of the hidrocarbons in air is not yet well understood.

In 1967 Newhall and Starkmann[1(*)], discussed the well known fact that the NO concentration at the exhaust is considerably higher than the corresponding value for equilibrium conditions.

Utilizing the Zeldovich reaction model:

$$\begin{aligned} O + N_2 &\rightleftarrows NO + N \\ N + O_2 &\rightleftarrows NO + O \end{aligned} \qquad (1)$$

and assuming that the O and N atoms are in equilibrium with their molecules throughout the reaction process, they shown that chemical species become frozen at the condition corresponding to maximum temperature.

In 1970, Lavoie et al[2], proposed the following reaction model:

$$\begin{aligned} O + N_2 &\rightleftarrows NO + N \\ N + O_2 &\rightleftarrows NO + O \\ N + OH &\rightleftarrows NO + H \\ H + N_2O &\rightleftarrows N_2 + OH \\ O + N_2O &\rightleftarrows N_2 + O_2 \\ O + N_2O &\rightleftarrows NO + NO \end{aligned} \qquad (2)$$

which was utilized in order to study the formation and evolution of nitrogen oxides. They assumed that species O , H , O_2 , and N_2 were in equilibrium and that species N and N_2O were in steady state.

They concluded that except in the case of combustion of lean mixtures at low temperature, the mechanism of formation of NO could be explained by the first three reaction of model (2), which is the Zeldovich's extended model.

Other investigators have directed their studies to the formation of NO in hydrogen-air flames, in which theoretical treatments are more precise because chemical kinetics of the hydrogen-air reaction is better understood.

In 1970 Bowmann[3], studied this case, comparing experimental results with those theoretically obtained utilizing a reaction model comprising 32 elementary reactions. He concluded that NO formation might be deduced from Zeldovich's model, if appro-

(*) All references are given at the end of the paper.

priated values for the O concentrations were utilized and not those corresponding to equilibrium conditions, showing experimentally that those O concentrations at the flame were considerably higher than those predicted by equilibrium conditions.

In 1970, Fenimore[4], suggested that the high velocity of NO formation, leading to what he called "prompt NO", was not compatible with Zeldovich's reaction model. Recently, Sarofim and Pohl[5] published a paper supporting Bowmann's conclusion, and on the other hand, Iverach and al[6] have lately published another paper supporting Fenimore's position.

In the present work an analytical study of NO formation in hydrogen-air flames is performed. The reaction model will comprise 34 elementary reactions and will be in a large part similar to that of Bowmann. However, the problem will be solved analytically by means of asymptotic methods, whereas Bowmann solved the problem numerically.

Analytical solutions allow the study of the influence of the parameters relevant to the process, showing for the present problem that the reactions proceed at each stage of the evolution. Such solutions may also lead to over-all expressions for the reaction rate and the NO rate of formation.

The theoretical treatment will be similar to that utilized by Liñán and Urrutia[7], for the study of the H_2-O_2 flame at supersonic conditions; and it is similar also to the study performed by Urrutia[8] and Sanmartin[9] for the analysis of the thermal decomposition of hydrazine. This theoretical treatment is based on the fact that the rate constants of the elementary reactions may differ from each other in several orders of magnitude, conditions which make feasible the solution of the problem by means of asymptotic expansions.

Reaction rates depend not only on rate constants but also on concentrations,so that as these evolve in time different reactions will become successively predominant. Thus there will exist several combustion stages and each of those stages will have different and appropriate reaction models.

The complete work is very extensive and only fundamental parts of it will be presented in this paper.

This part corresponds to the attainment of analytical expressions giving the over-all reaction rate and the rate of formation of NO at given pressure and temperature, which will be taken as constant, and as functions of the initial conditions of the mixture. These expressions would permit calculation of NO variation as function of time in an adiabatic combustion process, for given initial conditions.

It may be pointed out that hydrogen has presently a great interest as a potential fuel, and that in this case nitrogen oxydes are the only contaminants originated.

Hydrogen has a much greater flame velocity than that of hydrocarbons, and therefore, combustors designs will be differ-

TABLE I

$$K = AT^{B} \exp -\left(\frac{E}{RT}\right)$$

	reaction	direct A	direct B	direct E	inverse A	inverse B	inverse E	reference
1	$H_2 + OH \rightleftarrows H_2O + H$	2.19×10^{13}	0	5150	4.858×10^{14}	.2	20727	Baulch
2	$O_2 + H \rightleftarrows OH + O$	2.24×10^{14}	0	16800	6.647×10^{11}	.39	-469	"
3	$H_2 + O \rightleftarrows OH + H$	1.74×10^{13}	0	9450	7.737×10^{12}	0	7467	"
4	$H_2O+O \rightleftarrows OH + OH$	5.75×10^{13}	0	18000	1.169×10^{12}	.2	-444	"
5	$H + H + M \rightarrow H_2+M$	5×10^{18}	-1.15	0	-	-	-	
6	$O + O + M \rightarrow O_2+M$	4.7×10^{15}	-.28	0	-	-	-	
7	$O + H + M \rightarrow OH+M$	5.3×10^{15}	0	-2780	-	-	-	
8	$H+OH + M \rightarrow H_2O+M$	1.17×10^{17}	0	0	-	-	-	
9	$NO + N \rightleftarrows N_2 + O$	3×10^{13}	0	334	6.19×10^{13}	.1	75241	"
10	$NO + O \rightleftarrows N + O_2$	3.66×10^{8}	1.16	37847	6.43×10^{9}	1	6250	"
11	$NO + NO \rightleftarrows N_2O + O$	10^{14}	0	76600	2.5×10^{13}	0	27080	"
12	$NO + M \rightleftarrows N + O + M$	4×10^{20}	-1.5	150000	4.49×10^{18}	-.116	-2000	"
13	$N_2O+H \rightleftarrows N_2 + OH$	3×10^{13}	0	5420				
14	$N + OH \rightleftarrows NO + H$	4×10^{13}	0	0				Schofield
15	$O+N_2O \rightleftarrows N_2 + O_2$	3.61×10^{13}	0	24168				Campbell
16	$H_2 + O_2 \rightleftarrows 2OH$	2.5×10^{12}	0	39300				Bowman
17	$N_2 + M \rightleftarrows N + M + M$	7×10^{19}	-1	226600				Prud'homme

rent. In addition, adiabatic flame temperatures are much higher than those of hydrocarbons, and probably lean mixtures will have to be utilized in practical applications.

Due to these facts the study has been carried out for three temperature regions: 1000°K, 2000°K and 3000°K. Regarding pressure values the analysis is confined to values comprised between 2.9 and 39.2 bars, which are the normal operational values encountered in gas turbines.

A detailed analysis will be presented for T = 1000°K, and a brief discussion for T = 2000 and 3000°K.

Kinetic Scheme

We shall assume that the kinetic mechanism for the combustion of H_2 in air consists of 34 elementary reactions given in Table 1, which also includes corresponding rate constants. This kinetic scheme is quite similar to that used by Bowmann[3]. We consider homogeneous reaction at constant pressure P and temperature T.

If N_i is the number of moles of species i and V is the volume of the system the equation of evolution for each species is given by

$$\frac{1}{V}\frac{dN_i}{dt} = \sum_j r_j^i$$

where r_j^i is the rate of formation of species i due to reaction j. *As it is well known, for a mixture of ideal gases at constant* P and T,

$$\frac{d\left(\frac{N_i}{V}\right)}{dt} \equiv \frac{dn_i}{dt} = \sum_j r_j^i - \frac{n_i}{n_T}\sum_{i'}\sum_{j'} r_{j'}^{i'} \qquad (3)$$

where $n_T = \sum_i n_i = (n_T)_o$.

System (3) is to solved subject to the initial conditions

$$n_{H_2} = (n_{H_2})_o$$
$$n_{O_2} = (n_{O_2})_o$$
$$n_{N_2} = (n_{N_2})_o$$

and $(n_i)_o = 0$ for all other species.

From conservation of number of atoms of O, N and H two integrated relations (note that V is not conserved) can be obtained:

$$\frac{2n_{H_2} + 2n_{H_2O} + n_H + n_{OH}}{2n_{N_2} + 2n_{N_2O} + n_N + n_{NO}} = \frac{(n_{H_2})_o}{(n_{N_2})_o}$$

$$\frac{2n_{O_2} + n_{H_2O} + n_O + n_{OH} + n_{N_2O} + n_{NO}}{2n_{N_2} + 2n_{N_2O} + n_n + n_{NO}} = \frac{(n_{O_2})_o}{(n_{N_2})_o} \qquad (4)$$

A third integrated relation follows from the constants of T and P,

$$\Sigma n_i = (n_T)_o \quad . \tag{5}$$

If equations (4) and (5) are taken into account of the ten equations of system (3) (those for species O, H, OH, H_2O, N, NO and N_2O say) need be considered.

To make these equations dimensionless we define

$$x_i = \frac{n_i}{n_T} \quad , \quad \tau = n_T K_{2in} t \quad , \quad k_j = \frac{K_j}{K_{2in}} \quad . \tag{6}$$

We then obtain

$$\frac{dx_O}{d\tau} = \{k_{2d}x_{O_2}x_H - x_{OH}x_O\} - \{k_{3d}x_{H_2}x_O - k_{3i}x_{OH}x_H\} - \{k_{4d}x_{H_2O}x_O - k_{4i}x_{OH}^2\}$$
$$- 2k_{6d}n_T x_O^2 - \{k_{7d}n_T x_O x_H - k_{7i}x_{OH}\} + \{k_{9d}x_{NO}x_N - k_{9i}x_{N_2}x_O\}$$
$$- \{k_{10d}x_{NO}x_O - k_{10i}x_{O_2}x_N\} + \{k_{11d}x_{NO}^2 - k_{11i}x_{N_2O}x_O\}$$
$$+ \{k_{12d}x_{NO} - k_{12i}n_T x_O x_N\} - k_{15d}x_O x_{N_2O} - x_O\sigma$$

$$\frac{dx_H}{d\tau} = \{k_{1d}x_{H_2}x_{OH} - k_{1i}x_{H_2O}x_H\} - \{k_{2d}x_{O_2}x_H - x_{OH}x_O\} + \{k_{3d}x_{H_2}x_O - k_{3i}x_{OH}x_H\}$$
$$- 2\{k_{5d}n_T x_H^2\} - \{k_{7d}n_T x_O x_H - k_{7i}x_{OH}\} - \{k_{8d}n_T x_H x_{OH} - k_{8i}x_{H_2O}\}$$
$$- \{k_{13d}x_{N_2O}x_H - k_{13i}x_{N_2}x_{OH}\} + \{k_{14d}x_N x_{OH} - k_{14i}x_{NO}x_H\} - x_H\sigma$$

$$\frac{dx_{OH}}{d\tau} = -\{k_{1d}x_{H_2}x_{OH} - k_{1i}x_{H_2O}x_H\} + \{k_{2d}x_{O_2}x_H - x_{OH}x_O\}$$
$$+ \{k_{3d}x_{H_2}x_O - k_{3i}x_{OH}x_H\} + 2\{k_{4d}x_{H_2O}x_O - k_{4i}x_{OH}^2\} + \{k_{7d}n_T x_O x_H - k_{7i}x_{OH}\}$$
$$- \{k_{8d}n_T x_H x_{OH} - k_{8i}x_{H_2O}\} + \{k_{13d}x_{N_2O}x_H - k_{13i}x_{N_2}x_{OH}\}$$
$$- \{k_{14d}x_N x_{OH} - k_{14i}x_{NO}x_H\} + 2\{k_{16d}x_{H_2}x_{O_2} - k_{16i}x_{OH}^2\} - x_{OH}\sigma$$

$$\frac{dx_{H_2O}}{d\tau} = \{k_{1d}x_{H_2}x_{OH} - k_{1i}x_{H_2O}x_H\} - \{k_{4d}x_{H_2}x_O - k_{4i}x_{OH}^2\}$$
$$+ \{k_{8d}n_T x_H x_{OH} - k_{8i}x_{H_2O}\} - x_{H_2O}\sigma$$

$$\frac{dx_N}{d\tau} = -\{k_{9d}x_{NO}x_N - k_{9i}x_{N_2}x_O\} + \{k_{10d}x_{NO}x_O - k_{10i}x_N x_{O_2}\}$$
$$+ \{k_{12d}x_{NO} - k_{12i}n_T x_O x_N\} - \{k_{14d}x_N x_{OH} - k_{14i}x_{NO}x_H\} - 2k_{17i}n_T x_N^2 - x_N\sigma$$

$$\frac{dx_{NO}}{d\tau} = -\{k_{9d}x_{NO}x_N - k_{9i}x_{N_2}x_O\} - \{k_{10d}x_{NO}x_O - k_{10i}x_N x_{O_2}\}$$
$$- 2\{k_{11d}x_{NO}^2 - k_{11i}x_{N_2O}x_O\} - \{k_{12d}x_{NO} - k_{12i}n_T x_O x_N\}$$
$$+ \{k_{14d}x_N x_{OH} - k_{14i}x_{NO}x_H\} - x_{NO}\sigma$$

$$\frac{dx_{N_2O}}{d\tau} = \{k_{11d}x_{NO}^2 - k_{11i}x_{N_2O}x_O\} - \{k_{13d}x_{N_2O}x_H - k_{13i}x_{N_2}x_{OH}\}$$
$$- k_{15d}x_{N_2O}x_O - x_{N_2O}\sigma \qquad (7)$$

$$\frac{2x_{H_2O} + 2x_{H_2} + x_H + x_{OH}}{2x_{N_2} + 2x_{N_2O} + x_N + x_{NO}} = \frac{(x_{H_2})_o}{(x_{N_2})_o}$$

$$\frac{2x_{O_2} + x_{H_2O} + x_O + x_{OH} + x_{N_2O} + x_{NO}}{2x_{N_2} + 2x_{N_2O} + x_N + x_{NO}} = \frac{(x_{O_2})_o}{(x_{N_2})_o}$$

$$\Sigma x_i = 1 \qquad (8)$$

where $\sigma = (n_T^2 K_{2in})^{-1} \sum_i \sum_j r_j^i$

If we consider the values of k_j as taken from Table 1 at different T it can be observed that, in general, they differ from each other in several orders of magnitude. To take advantage of this fact in order to carry out an asymptotic analysis of equations (7) and (8) we shall introduce the small parameter ε, taken here to be 10^{-2}, and express all k_j in powers of ε. Formally we shall let ε go to zero although at the end of the analysis we shall set, for numerical purposes, $\varepsilon = 10^{-2}$.

As the dependency of k_j on T is very strong for many values of j, several ranges of T should be considered. We shall study temperatures around 1000°K in next Section, and temperatures around 2000 and 3000°K in the following one. As the dependency of system (7) on P (through the factor n_T) is much weaker, it appears that considering, for instance, pressures around 11.8 bars the asymptotic results should be valid for the entire interval from say 2.9-39.2 bars As far as $(x_{H_2})_o$, $(x_{O_2})_o$, $(x_{N_2})_o$ are concerned we shall assume that all three are of order of unity.

NO Formation around 1000°K

For T and P around 1000°K and 11.8 bars respectively we have

$$n_T = O(\varepsilon^2) \qquad (9)$$

and

$$
\begin{aligned}
k_{1d} &= O(\varepsilon^{1/2}) & k_{1i} &= O(\varepsilon^{3/2}) \\
k_{2d} &= O(\varepsilon^{3/2}) & k_{2i} &= O(1) \\
k_{3d} &= O(\varepsilon) & k_{3i} &= O(\varepsilon) \\
k_{4d} &= O(\varepsilon^{2}) & k_{4i} &= O(\varepsilon^{1/2}) \\
k_{5d} &= O(\varepsilon^{-1}) & & \text{——} \\
k_{6d} &= O(\varepsilon^{-1/2}) & & \text{——} \\
k_{7d} &= O(\varepsilon^{-3/2}) & & \text{——} \\
k_{8d} &= O(\varepsilon^{-2}) & & \text{——} \\
k_{9d} &= O(1) & k_{9i} &= O(\varepsilon^{8}) \\
k_{10d} &= O(\varepsilon^{5}) & k_{10i} &= O(\varepsilon) \\
k_{11d} &= O(\varepsilon^{8}) & k_{11i} &= O(\varepsilon^{3}) \\
k_{12d} &= O(\varepsilon^{15}) & k_{12i} &= O(\varepsilon^{-1}) \\
k_{13d} &= O(\varepsilon^{1/2}) & k_{13i} &= O(\varepsilon^{17/2}) \\
k_{14d} &= O(\varepsilon^{1/2}) & k_{14i} &= O(\varepsilon^{5}) \\
k_{15d} &= O(\varepsilon^{5/2}) & & \text{——} \\
k_{16d} &= O(\varepsilon^{5}) & & \text{——}
\end{aligned}
\qquad (10)
$$

Initially, at $\tau = 0$, all x_i vanish except for $i = H_2$, O_2 and N_2. It follows then from equations (7) - (10) that for small enough times equations (4) reduce (retaining dominant terms only) to

$$
\begin{aligned}
\frac{dx_O}{d\tau} &\simeq k_{2d} x_{O_2} x_H & \frac{dx_N}{d\tau} &\simeq k_{9i} x_{N_2} x_O \\
\frac{dx_H}{d\tau} &\simeq k_{1d} x_{H_2} x_{OH} & \frac{dx_{NO}}{d\tau} &\simeq k_{9i} x_{N_2} x_O \\
\frac{dx_{OH}}{d\tau} &\simeq 2k_{16d} x_{H_2} x_{O_2} & \frac{dx_{N_2O}}{d} &\simeq k_{13i} x_{N_2} x_{OH} \\
\frac{dx_{H_2O}}{d\tau} &\simeq k_{1d} x_{H_2} x_O
\end{aligned}
$$

Then, for small enough τ, we find

$$x_O = O(\varepsilon^7\tau^3) \qquad x_N = O(\varepsilon^{15}\tau^4)$$

$$x_H = O(\varepsilon^{5.5}\tau^2) \qquad x_{NO} = O(\varepsilon^{15}\tau^4)$$

$$x_{OH} = O(\varepsilon^5\tau) \qquad x_{N_2O} = O(\varepsilon^{13.5}\tau^2)$$

$$x_{H_2O} = O(\varepsilon^{5.5}\tau^2)$$

while x_{H_2} , x_{O_2} and x_{N_2} remain constant.

The above results describe what we might call the start-off or "zero" stage of the reaction. As x_i increases with τ some terms in equation (7) may change in order of magnitude and become dominant.

First stage

For $\tau = O(\varepsilon^{-1/2})$ a (first) stage develops in wich the equation for x_{OH} becomes

$$\frac{dx_{OH}}{d\tau} \simeq -k_{1d}x_{H_2}x_{OH} + 2k_{16d}x_{H_2}x_{O_2}$$

while other equations remain unchanged. It is obvious that for $\tau \gg \varepsilon^{-1/2}$ we obtain $x_{OH} = O(\varepsilon^{4.5})$ and therefore

$$x_O = O(\varepsilon^{6.5}\tau^2) \qquad x_N = O(\varepsilon^{14.5}\tau^3)$$

$$x_H = O(\varepsilon^5\tau) \qquad x_{NO} = O(\varepsilon^{14.5}\tau^3)$$

$$x_{H_2O} = O(\varepsilon^5\tau) \qquad x_{N_2O} = O(\varepsilon^{13}\tau)$$

Second stage

For $\tau = O(\varepsilon^{-1})$ the equations for x_O x_N and x_{NO} become

$$\frac{dx_O}{d\tau} \simeq k_{2d}x_{O_2}x_H - k_{3d}x_{H_2}x_O$$

$$\frac{dx_N}{d\tau} \simeq k_{9i}x_{N_2}x_O - k_{10i}x_{O_2}x_N$$

$$\frac{dx_{NO}}{d\tau} \simeq k_{9i}x_{N_2}x_O + k_{10i}x_{O_2}x_N$$

while x_{OH} is already in steady state given by

$$0 \simeq -k_{1d}x_{H_2}x_{OH} + 2k_{16d}x_{H_2}x_{O_2}$$

and the equations for the other species remain unchanged. Then *for* $\tau \gg \varepsilon^{-1}$ *we find*

$$x_O = O(\varepsilon^{5.5}\tau) \quad x_H = O(\varepsilon^5\tau) \quad x_{OH} = O(\varepsilon^{4.5}) \quad x_{H_2O} = O(\varepsilon^5\tau)$$

$$x_N = O(\varepsilon^{12.5}\tau) \quad x_{NO} = O(\varepsilon^{13.5}\tau) \quad x_{N_2O} = O(\varepsilon^{13}\tau)$$

Third stage

For $\tau = O(\varepsilon^{-3/2})$ equations for x_H becomes

$$\frac{dx_H}{d\tau} \simeq k_{1d}x_{H_2}x_{OH} - k_{2d}x_{O_2}x_H + k_{3d}x_{H_2}x_O$$

while x_O , x_{OH} , x_N are in steady state:

$$0 \simeq k_{2d}x_{O_2}x_H - k_{3d}x_{H_2}x_O$$

$$0 \simeq -k_{1d}x_{H_2}x_{OH} + 2k_{16d}x_{H_2}x_{O_2} + k_{2d}x_{O_2}x_H + k_{3d}x_{H_2}x_O$$

$$0 \simeq k_{9i}x_{N_2}x_O - k_{10i}x_{O_2}x_N$$

For $\tau \gg \varepsilon^{-3/2}$ we arrive at

$$x_O = O(\varepsilon^4 e^{c\varepsilon^{1.5}\tau}) \qquad x_N = O(\varepsilon^{11} e^{c\varepsilon^{1.5}\tau})$$

$$x_H = O(\varepsilon^{3.5} e^{c\varepsilon^{1.5}\tau}) \qquad x_{NO} = O(\varepsilon^{10.5} e^{c\varepsilon^{1.5}\tau})$$

$$x_{OH} = O(\varepsilon^{4.5} e^{c\varepsilon^{1.5}\tau}) \qquad x_{N_2O} = O(\varepsilon^{11.5} e^{c\varepsilon^{1.5}\tau})$$

$$x_{H_2O} = O(\varepsilon^{3.5} e^{c\varepsilon^{1.5}\tau})$$

where $c \simeq O(1)$.

The above exponential growth would lead to a new stage for $e^{c\varepsilon^{1.5}\tau} = \frac{1}{\varepsilon}$, that is, for times only "slightly" larger than $\varepsilon^{-3/2}$ $\{\tau = O(\varepsilon^{-3/2}$, L $1/\varepsilon)\}$. In such case it is simplest to just modify this third stage by retaining the new terms that would become dominant if the exponential growth were to remain unchecked. The modified equations are

$$\frac{dx_H}{d\tau} \simeq k_{1d}x_{H_2}x_{OH} - k_{2d}x_{O_2}x_H + k_{3d}x_{H_2}x_O - 2k_{5d}n_T x_H^2 - k_{7d}n_T x_O x_H - k_{8d}n_T x_H x_{OH}$$

$$\frac{dx_{H_2O}}{d\tau} \simeq k_{1d}x_{H_2}x_{OH} + k_{8d}n_T x_H x_{OH}$$

$$\frac{dx_{N_2O}}{d\tau} \simeq k_{13i}x_{N_2}x_{OH} - k_{13d}x_H x_{N_2O}$$

while for x_O and x_{OH}

$$0 \simeq k_{2d}x_{O_2}x_H - k_{3d}x_{H_2}x_O - k_{7d}n_T x_O x_H$$

$$0 \simeq -k_{1d}x_{H_2}x_{OH} + k_{2d}x_{O_2}x_H + k_{3d}x_{H_2}x_O + k_{7d}n_T x_O x_H - k_{8d}n_T x_H x_{OH} + 2k_{16d}x_{H_2}x_{O_2}$$

So that for $\tau >> \varepsilon^{-3/2}$

$$x_O = O(\varepsilon) \qquad x_H = O(\varepsilon^{1/2}) \qquad x_{OH} = O(\varepsilon^{3/2}) \qquad x_{H_2O} = O(\varepsilon^2\tau)$$

$$x_N = O(\varepsilon^8) \qquad x_{NO} = O(\varepsilon^9\tau) \qquad x_{N_2O} = O(\varepsilon^9)$$

Final stage

From the above equations it follows that for $\tau = O(\varepsilon^{-2})$ x_{H_2O} becomes of order of unity so that from equation (8) it can be seen that x_{H_2}, x_{O_2} and x_{N_2} cannot be further retained equal to their initial values. Then the final equations are

$$\frac{dx_{H_2O}}{d\tau} \simeq k_{1d}x_{H_2}x_{OH} - k_{1i}x_{H_2O}x_H + k_{8d}n_T x_H x_{OH} + x_{H_2O}k_{2d}x_{O_2}x_H$$

$$\frac{dx_{NO}}{d\tau} \simeq k_{9i}x_{N_2}x_O + k_{10i}x_{O_2}x_N + x_{NO}k_{2d}x_{O_2}x_H$$

the species O, H, OH, N and N_2O being in steady state

$$0 \simeq k_{2d}x_{O_2}x_H - k_{3d}x_{H_2}x_O - k_{7d}n_T x_O x_H$$

$$0 \simeq k_{1d}x_{H_2}x_{OH} - k_{1i}x_{H_2O}x_H - k_{2d}x_{O_2}x_H + k_{3d}x_{H_2}x_O - 2k_{5d}n_T x_{OH}^2 - k_{7d}n_T x_O x_H - k_{8d}n_T x_H x_{OH}$$

$$0 \simeq -k_{1d}x_{H_2}x_{OH} + k_{1i}x_{H_2O}x_H + k_{2d}x_{O_2}x_H + k_{3d}x_{H_2}x_O + k_{7d}n_T x_O x_H - k_{8d}n_T x_H x_{OH}$$

$$0 \simeq k_{9i}x_{N_2}x_O - k_{10i}x_{O_2}x_N$$

$$0 \simeq -k_{13d}x_{N_2O}x_H + k_{13i}x_{N_2}x_{OH}$$

We also have

$$\frac{x_{H_2} + x_{H_2O}}{x_{N_2}} = \frac{(x_{H_2})_o}{(x_{N_2})_o} \equiv \alpha \ , \ \frac{2x_{O_2} + x_{H_2O}}{2x_{N_2}} = \frac{(x_{O_2})_o}{(x_{N_2})_o} \equiv \beta$$

$$x_{H_2} + x_{O_2} + x_{N_2} + x_{H_2O} = 1$$

This system leads to the following equation for x_H

$$k_{5d}n_T x_H^2 + k_{8d}n_T x_H^2 \frac{k_{1i}x_{H_2O} + 2k_{2d}x_{O_2}}{k_{1d}x_{H_2} + k_{8d}n_T x_{OH}} - k_{3d}x_{H_2} \frac{k_{2d}x_{O_2}x_H}{k_{3d}x_{H_2} + k_{7d}n_T x_H} = 0$$

The only positive root of this equation is given, within a few per cent, by

$$x_H = \frac{k_{3d}}{2k_{7d}n_T} x_{H_2} \frac{x_{H_2} + ax_{H_2O} + bx_{O_2}}{x_{H_2}(1+c) + ax_{H_2O} + 2bx_{O_2}} \times \left[\sqrt{1 + 4b/c\, x_{O_2} \frac{x_{H_2}(1+c) + ax_{H_2O} + 2bx_{O_2}}{(x_{H_2} + ax_{H_2O} + bx_{O_2})^2}} - 1\right] \qquad (11)$$

where

$$a = \frac{k_{8d}k_{1i}}{k_{1d}k_{5d}} = .52\, T^{1.35}\, e^{-\frac{15577}{RT}}$$

$$b = \frac{k_{8d}k_{2d}}{k_{1d}k_{5d}} = .24\, T^{1.15}\, e^{-\frac{11650}{RT}}$$

$$c = \frac{k_{3d}k_{8d}}{k_{1d}k_{7d}} = 17\, e^{-\frac{7080}{RT}}$$

and

$$x_{H_2} = (2 + x_{H_2O}) \frac{\alpha}{2(1+\alpha+\beta)} - x_{H_2O}$$

$$x_{O_2} = (2 + x_{H_2O}) \frac{\beta}{2(1+\alpha+\beta)} - \frac{x_{H_2O}}{2} \qquad (12)$$

$$x_{N_2} = (2 + x_{H_2O}) \frac{1}{2(1+\alpha+\beta)}$$

We then find

$$\frac{dx_{H_2O}}{d\tau} = (2 + x_{H_2O})k_{2d}x_{O_2}x_H \qquad (13)$$

$$\frac{dx_{NO}}{d\tau} = \left(\frac{2k_{9i}\, x_{N_2}}{k_{3d}x_{H_2} + k_{7d}n_T x_H} + x_{NO}\right)k_{2d}x_{O_2}x_H \qquad (14)$$

we also find for the other species

$$x_O = \frac{k_{2d}x_{O_2}x_H}{k_{3d}x_{H_2} + k_{7d}n_T x_H} \quad , \quad x_{OH} = \frac{k_{1i}x_{H_2O}x_H + 2k_{2d}x_{O_2}x_H}{k_{1d}x_{H_2} + k_{8d}n_T x_H}$$

$$x_N = \frac{k_{9i}}{k_{10i}} x_{N_2} \frac{k_{2d} x_H}{k_{3d}x_{H_2} + k_{7d}n_T x_H} ,$$

$$x_{N_2O} = \frac{k_{13i}x_{N_2}}{k_{13d}} \frac{k_{1i}x_{H_2O} + 2k_{2d}x_{O_2}}{k_{1d}x_{H_2} + k_{8d}n_T x_H}$$

Equation (13) together with Eqs.(11) and (12) yield the overall reaction rate; Eq.(14) then yields the rate of formation of NO.

NO Formation around 2000°K and 3000°K

A similar mathematical analysis was performed in the regions around 2000°K and 3000°K.

At 2000°K the final state is governed by the following set of equations:

$$\frac{dx_{H_2O}}{d\tau} = k_{1d}x_{H_2}x_{OH} - k_{1i}x_{H_2O}x_H + k_{4i}x_{OH}^2 + k_{8d}n_T x_H x_{OH} + x_{H_2O}k_{8d}n_T x_H x_{OH}$$

$$\frac{dx_O}{d\tau} = k_{2d}x_{O_2}x_H - x_O x_{OH} - k_{3d}x_{H_2}x_O + k_{4i}x_{OH}^2 + x_O k_{8d}n_T x_H x_{OH}$$

$$\frac{dx_H}{d\tau} = k_{1d}x_{H_2}x_{OH} - k_{1i}x_{H_2O}x_H - k_{2d}x_{O_2}x_H + x_{OH}x_O + k_{3d}x_{H_2}x_O - k_{8d}n_T x_H x_{OH} + x_H k_{8d}n_T x_H x_{OH}$$

$$\frac{dx_{OH}}{d\tau} = -k_{1d}x_{H_2}x_{OH} + k_{1i}x_{H_2O}x_H + k_{2d}x_{O_2}x_H - x_{OH}x_O + k_{3d}x_{H_2}x_O - 2k_{4i}x_{OH}^2 - k_{8d}n_T x_H x_{OH} + x_{OH}k_{8d}n_T x_H x_{OH}$$

$$\frac{dx_{NO}}{d\tau} = 2k_{9i}x_{N_2}x_O + x_{NO}k_{8d}n_T x_{OH}$$

$$0 = k_{9i}x_{N_2}x_O - k_{14d}x_N x_{OH}$$

$$0 = -k_{13d}x_{N_2O}x_H + k_{13i}x_{N_2}x_{OH}$$

It may be seen that neither x_o nor x_H or x_{OH} are in steady state. Therefore, at this range of temperatures it appears

not feasible to obtain over-all reaction rates.

Around 3000°K the analysis shows that there are two initial stages such that at the end of the second one all species except x_{O_2}, x_{H_2}, x_{N_2} and x_{N_2O} present exponential growth. The introduction of new terms that become then dominants appear to lead after tedious mathematical considerations to the following final equations

$$\frac{dx_{H_2O}}{d\tau} = (2 + x_{H_2O})\, k_{8d} n_T x_{OH} x_H \tag{15}$$

$$0 = x_{OH} x_O - k_{2d} x_{O_2} x_H + k_{8d} n_T x_H x_{OH}$$

$$0 = k_{1i} x_{H_2O} x_H - k_{1d} x_{H_2} x_{OH} - k_{3d} x_{H_2} x_O$$

$$0 = k_{4i} x_{OH}^2 - k_{3d} x_{H_2} x_O - k_{4d} x_{H_2O} x_O$$

$$\frac{dx_{NO}}{d\tau} = 2k_{9i} x_{N_2} x_O + x_{NO} k_{8d} n_T x_{OH} x_H \tag{16}$$

$$0 = k_{9i} x_{N_2} x_O - k_{14d} x_N x_{OH}$$

$$\frac{dx_{N_2O}}{d\tau} = -k_{11i} x_{N_2O} x_O - k_{13d} x_{N_2O} x_H + k_{13i} x_{N_2} x_{OH} - k_{15d} x_O x_{N_2O}$$

$$+ x_{N_2O} k_{8d} n_T x_{OH} x_H$$

Equation (15) together with Eqs. (17)-(20) below yield the over-all reaction rate at 3000°K:

$$x_{OH} = \left[\frac{k_{1d} k_{2d} k_{3d}}{k_{1i} k_{4i}} \frac{(A - B x_{H_2O})(C - D x_{H_2O})}{x_{H_2O}} \left\{ C - D x_{H_2O} + \frac{k_{4d}}{k_{3d}} x_{H_2O} \right\} \right]^{1/2} \tag{17}$$

where

$$A = \frac{\beta}{1 + \alpha + \beta} \qquad B = \frac{1 + \alpha}{2(1 + \alpha + \beta)}$$

$$C = \frac{\alpha}{1 + \alpha + \beta} \qquad D = \frac{2 + \alpha + 2\beta}{2(1 + \alpha + \beta)} \tag{18}$$

α and β being $(x_{H_2}/x_{N_2})_o$ and $(x_{O_2}/x_{N_2})_o$ respectively, and

$$x_H = \frac{k_{4i}x_{OH}^3}{(k_{2d}x_{O_2})^2} \frac{k_{2d}x_{O_2} + k_{8d}n_T x_{OH}}{k_{3d}x_{H_2} + k_{4d}x_{H_2O}} \tag{19}$$

where

$$\begin{aligned} x_{O_2} &= A - B\, x_{H_2O} - x_{OH}/2 \\ x_{H_2} &= C - D\, x_{H_2O} - x_{OH}/2 \end{aligned} \qquad \frac{x_{OH}}{2} \tag{20}$$

Then Eq.(16) together with equations

$$x_{N_2} = 1 - x_{O_2} - x_{H_2} - x_{H_2O} - x_{OH}$$

$$x_O = \frac{k_{4i}x_{OH}^2}{k_{3d}x_{H_2} + k_{4d}x_{H_2O}}$$

applied the rate of formation of NO.

Conclusions

An analytical study of nitric oxide formation in H_2-air combustion has been performed, assuming both constant pressure and temperature.

The analysis shows that there are several stages in the combustion and it yields an appropriate reaction scheme for each stage.

Over-all reaction rate and rate of formation of NO have being obtained for temperatures around 1000 and 3000°K. These results may be directly applied to the calculation of NO formation in an adiabatic combustion process with given initial conditions.

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